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NAVORD REPORT

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HEAT RESISTANT EXPLOSIVES V

3-DIAMINO-2,4,6-TRINITROBENZENE, DATB, BY AMMONOLYSIS OF
METHOXYTRINITROBENZENE COMPOUNDS (C)

**FC
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15 DECEMBER 1958



U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

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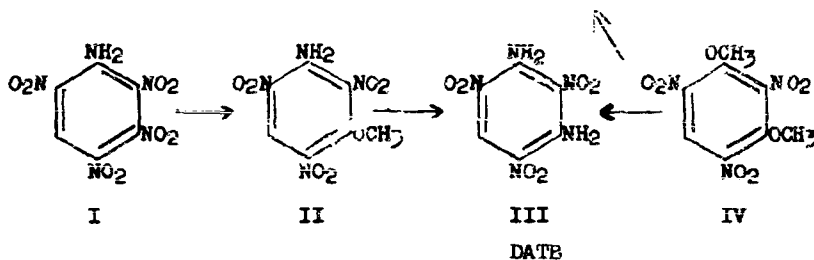
HEAT RESISTANT EXPLOSIVES V

1,3-Diamino-2,4,6-trinitrobenzene, DATB,
by Ammonolysis of Methoxytrinitrobenzene Compounds

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ABSTRACT: 1,3-Diamino-2,4,6-trinitrobenzene, DATB, was prepared in good yield from 2,3,4,6-tetranitroaniline, I, in two steps. 3-Methoxy-2,4,6-trinitroaniline, II, was obtained by the reaction of methanol with tetranitroaniline and converted directly to DATB, III, by adding the methanolic reaction solution to ammoniacal methanol. Alternatively DATB was obtained by the reaction of benzene or acetone solutions of crystalline 3-methoxy-2,4,6-trinitroaniline with ammoniacal methanol. Three different crystal habits were obtained depending upon reaction conditions. DATB in large rod shaped crystal habit was made by the addition of benzene solutions of 1,3-dimethoxy-2,4,6-trinitrobenzene, IV, to ammoniacal methanol.



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This report describes the preparation of 1,3-diamino-2,4,6-trinitrobenzene, DATB, by the ammonolysis of 3-methoxy-2,4,6-trinitroaniline and 1,3-dimethoxy-2,4,6-trinitrobenzene. NAVORD Report 6016 is the initial report describing the preparation and properties of DATB. Other recent reports concerning the latest work on this compound are NAVORD Reports 6203 and 6223.

This work was performed under Task FR-44, Explosive Synthesis, as part of a fundamental investigation of high temperature stable explosives.

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HEAT RESISTANT EXPLOSIVES V

1,3-Diamino-2,4,6-trinitrobenzene, DATB,
by Ammonolysis of Methoxytrinitrobenzene Compounds

INTRODUCTION

Current military explosives are unusable in high speed missile warheads because of decomposition induced by aerodynamic heating of the warhead. The Organic Chemistry Division has been investigating the synthesis of new high temperature resistant explosives which would function after being subjected to high temperatures for a short period of time. One of these, 1,3-diamino-2,4,6-trinitrobenzene, or DATB, was prepared and given a preliminary evaluation (1). The evaluation revealed that the compound was insensitive to impact and thermally stable at 500°F (260°C). A plastic bonded composition containing DATB with 5% binder had performance energy about equivalent to TNT. Because of these properties and the reasonable availability of DATB, there has been considerable military interest in it for special applications. Consequently this Division has been improving the synthesis and determining physical properties in support of the military program.

This report describes the synthesis of DATB from 3-methoxy-2,4,6-trinitroaniline and 1,3-dimethoxy-2,4,6-trinitrobenzene.

DISCUSSION AND RESULTS

1. DATB from 3-Methoxy-2,4,6-trinitroaniline. In the initial study, DATB was obtained principally by adding either a solution of tetranitroaniline in Cellosolve or the crude solid compound to ammonia in 50% methanol-water. The product obtained by this method had very good thermal stability but was obtained at the cost of using large volumes of solvent or, as an alternative, handling large quantities of the solid explosive intermediate. In an experiment involving the addition of solid tetranitroaniline into the ammoniacal methanol it was noted that the aniline stayed in solution for a few minutes before DATB precipitated. On the premise that the DATB was coming partially from nucleophilic substitution of 3-methoxy-2,4,6-trinitroaniline as well as from substitution of a nitro group by ammonia, some DATB was prepared by ammonolysis of pure methoxytrinitroaniline to determine how easily DATB may be obtained by a two-stage reaction of tetranitroaniline to methoxytrinitroaniline to DATB.

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Although initially the samples of DATB prepared in this way were not as thermally stable as the material obtained by direct ammonolysis of tetranitroaniline, the process was studied further and improved.

The intermediate 3-methoxy-2,4,6-trinitroaniline was readily prepared by heating a slurry of crude tetranitroaniline and methanol at reflux temperature for a few hours. The product either was isolated as fine light yellow needles, which melted within one degree of the melting point of pure methoxytrinitroaniline, or it was used immediately in solution in the ammonolysis step. The wine red reaction mother liquor contained side reaction products which probably resulted from reduction reactions occurring during the methoxy compound formation and from the reaction of methanol with by-products in the crude tetranitroaniline. However, the by-products did not interfere with the ammonolysis of the methoxytrinitroaniline and DATB with good thermal stability was made without isolating the intermediate. Fortunately the impurities from the tetranitroaniline preparation, from the preparation of the methoxytrinitroaniline, and from the ammonolysis itself remained in solution for the most part. The DATB was usually discolored somewhat when prepared by this two stage procedure but nonetheless had acceptable thermal stability.

The isolation of methoxytrinitroaniline served as an easy purification step which eliminated the accumulation of impurities from the crude tetranitroaniline and the methanolysis reaction. High yields of DATE of good purity, as shown by the vacuum stability test, were obtained by adding benzene or acetone solutions of the methoxy compound to aqueous ammonia in methanol. The reaction mother liquor was not deeply colored, and the DATE for the most part was a light yellow. An optimum procedure which evolved from a study of reaction conditions consisted of dissolving the methoxytrinitroaniline in acetone or benzene and adding this solution to aqueous ammonia in methanol at 50°C.

Much effort was expended in determining which reaction conditions would give crystal habits other than thin plates, and crystals large enough to be ground down to an optimum smaller size and distribution for plastic bonding. As expected, reaction conditions had some effect, but only three general types of crystals were obtained with assurance of reproduction; thin plates, twinned trapezoid shaped rods ("butterflies"), and equant pyramidal crystals. The former two habits ranged in

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size from 30-100 μ in the longer dimension, and 20-40 μ in the shorter. The experimental results evolved the following general observations:

(a) Crystals of a particular habit obtained on a small laboratory scale could not always be obtained upon scaling up, even though the procedure was repeated precisely.

(b) The presence of water appeared to be necessary to obtain larger crystals and to reduce the amount of reduction by-products.

(c) The addition of the methoxytrinitroaniline solutions to ammoniacal methanol rather than the reverse gave larger, better formed crystals.

(d) Best results were obtained at a reaction temperature of 50°C \pm 5°. No particular advantage was observed at higher temperatures and crystals of smaller particle size were obtained at lower temperatures. Rapid stirring and dilute reaction solutions permitted better crystal formation with fewer occlusions in the crystals.

(e) Vacuum thermal stability at 260°C did not correlate with either appearance or melting point. Good color and sharp melting point did not indicate that the material would have thermal stability within the specification limits. In general, DATB of the larger crystal sizes underwent more decomposition, probably because of crystal occlusions. The materials prepared in this study gave between 3.0 - 8.7 cc of gas per gram per hour at 260°C in the vacuum thermal stability test.

(f) Methoxytrinitroaniline was easier to prepare and use than ethoxy trinitroaniline.

2. DATB from 1,3-Dimethoxy-2,4,6-trinitrobenzene. On the basis of the methoxytrinitroaniline experience, the ammonolysis of 1,3-dimethoxy-2,4,6-trinitrobenzene (2) was carried out under the same conditions. The DATB from this intermediate was light lemon yellow and usually formed as long rods, some being 200-300 μ in length. Scaling up of the laboratory experiments was more successful in this case. As in the methoxytrinitroaniline systems, addition of a benzene solution of the dimethoxy compound to ammoniacal methanol worked better than the reverse addition.

EXPERIMENTAL

1. DATB from Tetranitroaniline Without Isolation of 3-Methoxy-2,4,6-trinitroaniline.

(a) A solution of 5 ml of concentrated aqueous ammonia in 100 ml of methanol was placed in a 500 ml creased, 3-necked, round bottom flask fitted with a mechanical stirrer and a dropping funnel. Crude tetranitroaniline, 10 g in 250 ml methanol, was converted to 3-methoxy-2,4,6-trinitroaniline by heating briefly at reflux with stirring. This solution was then added dropwise during one half hour to the methanol ammonia solution at 50°C. The solution became red and after about 3-5 minutes the first precipitate appeared. The reaction mixture was stirred for one half hour at 50°C after the addition of the methoxytrinitroaniline was completed. The product was filtered off, washed with methanol, and hot water and dried; yield, 7.2 g or 81%.

(b) A solution of 10 g crude tetranitroaniline in 250 ml methanol in a 500 ml creased, 3-neck, round bottom flask fitted with a mechanical stirrer and a reflux condenser was prepared by heating the mixture to reflux for one half hour. Ammonia gas was then admitted to the atmosphere above the solution. The solution became deep red in color at once and after two minutes a yellow crystalline precipitate began to form. The reaction mixture was stirred at reflux temperature for one half hour with frequent addition of ammonia gas above the mixture. The mixture was stirred one half hour after cooling and filtered. The product was washed well with hot water and finally with acetone; yield, 7.95 g, 89%. The crystals were triangular in shape with average particle size of about 40-60 microns on the side.

2. Preparation of 3-Methoxy-2,4,6-trinitroaniline. A slurry of 250 g crude tetranitroaniline and 1 liter of methanol in a 3 liter, 3-necked round bottom flask fitted with a thermometer, mechanical stirrer and reflux condenser was heated at reflux temperature for about an hour. Complete solution was not achieved, but the change in form of solid material from an amorphous solid to well formed needles was indicative of the completion of the reaction. The reaction mixture was cooled and the product was filtered off, washed with methanol and air dried. The yield of light yellow needles was 192 g or 77%; m.p. 134-5°C, uncorrected.

3. DATB from 3-Methoxy-2,4,6-trinitroaniline.

(a) A creased, 2-liter 3-neck round bottom flask with a mechanical stirrer and two dropping funnels, and containing 500 ml of methanol and heated to 50° C by a water bath was used for the reaction. A solution of 50 g of 3-methoxy-2,4,6-trinitroaniline in 250 ml of acetone was placed in one dropping funnel and a solution of 27.5 ml of concentrated aqueous ammonia in 212.5 ml of methanol was placed in another dropping funnel. A portion, 25 ml, of the methanol-ammonia solution first was added to the methanol in the flask. Then both solutions were added simultaneously and slowly during a two-hour period, always keeping the methanol-ammonia solution addition rate slightly faster than the methoxy aniline solution. Rapid, turbulent stirring was maintained during the reaction. The reaction mixture was stirred for one-half hour after completion of the addition; then the orange colored crystalline product was filtered off, washed with methanol and air dried. The yield was 38 g or 81%; m.p. 280-282°C. The crystalline particles were fines mixed with ill formed massive rounded crystals, "potato" shaped (Fig. 1).

(b) A solution of 10 ml of concentrated aqueous ammonia in 250 ml of methanol was placed in a 1-liter 3-neck creased round bottom flask with a mechanical stirrer and dropping funnel. A solution of 10 g of 3-methoxy-2,4,6-trinitroaniline dissolved in 250 ml of benzene was added dropwise during one hour while maintaining the temperature at 50°C. The reaction mixture was stirred for one hour after the addition of the methoxy aniline solution was complete and then the product was filtered off, washed with methanol and air dried. It was an orange yellow crystalline material, shaped like thick rods but somewhat agglomerated (Fig. 2). The yield was 8.5 g, 90%; m.p. 282-284°C.

(c) A solution of 10 g 3-methoxy-2,4,6-trinitroaniline in 150 ml of methanol was prepared by warming on a steam bath. Ammonia gas was bubbled into this solution, kept warm on the steam bath. The solution turned cherry red immediately on addition of the gas and a yellow precipitate began to form in 2-3 minutes. Precipitation was complete in about 15 minutes. The solution was allowed to cool with occasional shaking. The product was filtered off, washed with methanol, acetone, and water and dried in an oven at 60°C. The yield of yellow crystalline product was 9.0 g or 95.8%. The crystals were a mixture of rods and triangles, all thin plates.

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4. DATB from 1,3-Dimethoxy-2,4,6-trinitroaniline. A solution of 150 ml of concentrated aqueous ammonia in three liters of methanol was placed in the flask and heated to 50°C. A solution of 200 g of 1,3-dimethoxy-2,4,6-trinitrobenzene in 1200 ml of benzene was added during 90 minutes with stirring. The temperature varied between 50° and 65°C. Precipitation of the product started about three minutes after the addition was begun. The reaction mixture was stirred for an additional 30 minutes at 50°C, the product was then collected on a Buchner funnel and washed with methanol. After air drying the product weighed 165 g, and consisted of lemon yellow, well formed rods, typically 80 x 200μ (Fig. 3). A small portion of the product was dried at 100°C in a vacuum oven and the physical properties were measured; m.p. 283-285°C, uncorrected, thermal stability at 250°C for two hours = 2.4 cc/g/hr.

A scaled up preparation by this method used 755 g of 1,3-dimethoxy-2,4,6-trinitrobenzene and pilot plant conditions (an open stainless steel, jacketed reaction vessel equipped with an efficient stirrer) and yielded 557 g of product, 78%, which had the following properties: m.p. 283.5-284.5°C, uncorrected, bulk density 0.43 g/cc, thermal stability at 260°C for two hours = 3.6 g/cc/hr.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of others in carrying out this study. H. T. Simmons and Alvin H. Rosen made the vacuum thermal stability measurements. The 1,3-dimethoxy-2,4,6-trinitrobenzene was kindly furnished by M. J. Kamlet and J. C. Dacons. Francis Taylor, Jr., aided in the large scale preparation of DATB from dimethoxytrinitrobenzene.

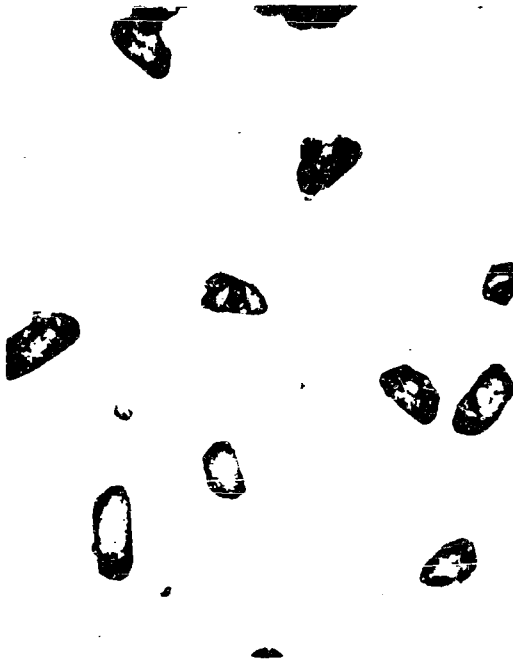


FIG. 1 DATB FROM ACETONE SOLUTION OF 3-METHOXY-
2,4,6-TRINITROANILINE ADDED TO AMMONIACAL
METHANOL [100X]



FIG. 2 DATB FROM BENZENE SOLUTION OF 3-METHOXY-
2,4,6 - TRINITROANILINE ADDED TO AMMONIACAL
METHANOL [100X]

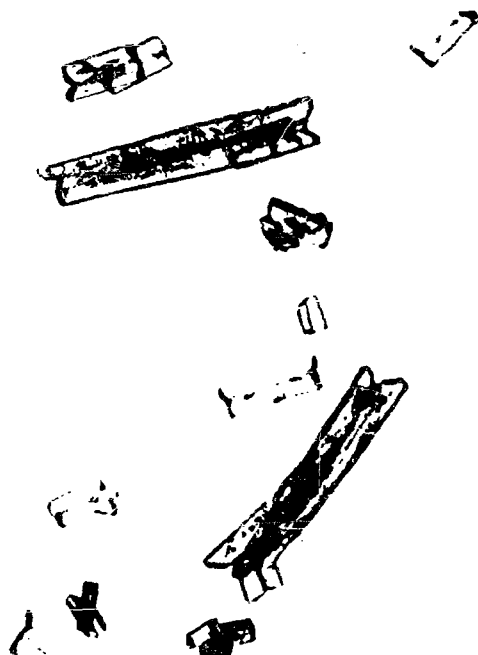


FIG. 3 DATB FROM BENZENE SOLUTION OF 1,3-DIMETHOXY-
2,4,6-TRINITROBENZENE ADDED TO AMMONIACAL
MENTHANOL [100X]

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